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Destruction of PCBs (Polychlorinated Biphenyls). Environmental Applications of Alkali Metal Polyethylene Glycolate Complexes

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DESTRUCTION OF PCBs - ENVIRONMENTAL APPLICATIONS OF ALKALI METAL POLYETHYLENE GLYCOLATE COMPLEXES

by

Frank J. Iaconianni
Franklin Research Center
Philadelphia, Pennsylvania 19103

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Project Officer

Charles J. Rogers
Alternative Technologies Division
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

This project is a follow-on to a study which focused primarily on the feasibility of chemical detoxification of soil using FRCs NaPEG Reagents. The fundamental chemistry of the decomposition of PCBs was also investigated in the previous study. The research described herein involved primarily a laboratory study of treatment methods for PCB contaminated soil using the most effective NaPEG Reagents in terms of reactivity and stability.

In the first phase, experiments using soils contaminated in the laboratory were resumed; experimental conditions and procedures were greatly revised in light of earlier results. This phase of testing was directed toward demonstrating that the concentration of PCBs in soil can be reduced to below 50 ppm by direct addition of the NaPEG Reagent under ambient conditions typical of an in-situ treatment of a spill.

Laboratory tests during the second phase centered on the treatment of PCB contaminated soil obtained from Buffalo, N.Y. and Philadelphia, PA. The effects of variable reaction parameters were examined in detail.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important enviornmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the application of alkali metal polyethylene glycolate complexes to the destruction of PCBs in the environment and will be useful to the U. S. Environmental Protection Agency.

For further information, please contact the (Division) of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratry

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ABSTRACT

The project described in this report is a follow-on to that study which focused primarily on the feasibility of chemical detoxification of soil using FRC's NaPEG Reagents. The fundamental chemistry of the decomposition of PCBs was also investigated in the previous study. The research described herein involved primarily a laboratory study of treatment methods for PCB-contaminated soil using the most effective NaPEG Reagents, in terms of reactivity and stability. The study was aimed at identifying treatment conditions necessary for the most efficient decontamination in a direct field application. On-site and off-site field verification studies were also conducted using PCB-contaminated soil from spills in Buffalo, NY and in Philadelphia, PA.

In the first phase of this study, experiments using soils contaminated in the laboratory were resumed; experimental conditions and procedures were greatly revised in light of earlier results. This phase of testing was directed primarily toward demonstrating that the concentration of PCBs in soil can be reduced to below 50 ppm by direct addition of the NaPEG reagent under ambient conditions typical of an in-situ treatment of a spill.

Laboratory tests conducted during the second phase of this project centered mainly on the treatment of PCB-contaminated soil obtained from the two spill sites. The effects of variable reaction parameters which affect the rate of decontamination were examined in detail.

ACKNOWLEDGMENT

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SECTION 1

INTRODUCTION

The enormous variety and amount of toxic halogenated organic materials which have pervaded our environment during the past fifty years have left us with major, crucial problems of disposal. These problems were clearly delineated in a recent USEPA publication, "State-of-the Art Report: Pesticide Disposal Research[1]." The accumulation of polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs, "dioxins") in soil, sand, and living tissue is a serious problem that has received considerable public attention in recent years. Although a great amount of work has been done by many groups in the area of direct chemical decomposition of these and other halogenated organics, relatively little effort has been directed toward in situ chemical detoxification.

The "clean up" of a contaminated site, usually volves landfilling, and is not really a permanent detoxification but rather a transfer of a toxic spill from one region to another. Landfilled toxic materials are still in the environment and will persist there until they are chemically destroyed. Our past and current research in the area of chemical detoxification is addressed to the well-known extreme chemical stability of chlorinated aromatics[2] since these comprise the bulk of the problematic halogenated types.

In the chemistry laboratory at the Franklin Research Center (FRC) during the summer of 1978 a new chemical reagent was synthesized and used to effectively dechlorinate PCB oils. Since that time a series of reagents have been developed and are now called NaPEG[tm] Reagents. They are essentially alkali metal polyethylene glycolates which produce rapid dehalogenation of halo-organic compounds of all types--in open air systems.

The aerobic nature of the NaPEG System immediately suggested its potential for use on hazardous chemical spills. In August of 1979 the U.S. EPA provided grant support to investigate the chemistry underlying the dehalogenation process, concentrating on dechlorination of PCBs. Subsequent EPA grant assistance was provided for a limited field study of the effects of a NaPEG reagent on PCB-contaminated soil. This research was described in a Project Summary Report entitled "Dehalogenation of PCBs Using New Reagents prepared from Sodium Polyethylene Glycolate-Application to PCB Spills and Decontaminated Soils", dated August 31, 1982.

Additional EPA grant assistance was awarded in 1982 for the detailed investigation of the effects of variable reaction parameters on the rate and extent of chemical decontamination of the substrate. This research focussed almost exclusively on the direct chemical treatment of PCB-contaminated soil. The continued laboratory investigation was aimed at identifying treatment conditions necessary for the most efficient decontamination in a direct field application. During the study an optimum reagent composition was selected based on chemical considerations. Maximum reactivity toward PCBs and other halogenated organics coupled with minimum sensitivity to reagent-deactivating side reactions was sought in selecting the best reagent formulation for further study. This report describes the research performed the results obtained.

SECTION 2
CONCLUSIONS

The results of the overall study clearly show that the NaPEG Reagents can significantly reduce the concentration of PCBs in contaminated soils under controlled laboratory conditions. There are, however, several areas in which improvement and optimizaton must be done in order to develop a viable and economical process for chemically treating PCB-contaminated soils in the field. The most recent results of laboratory experiments suggest that this is indeed possible.

EARLY EXPERIMENTS

The study described herein commenced with the completion of ongoing laboratory experiments using simulated soil substrates spiked with PCBs. Results of these tests confirmed dramatically that PCBs are dechlorinated by the NaPEG Reagents under mild, ambient conditions. Subsequent early experiments using actual soils spiked with PCBs clearly show, however, that water, particularly water in soil, greatly reduces the rate of dechlorination, and hence reduces the effectiveness of the reagents to PCBs in real soils. These adverse effects were, in fact, greater than expected from the preliminary results obtained in previous studies. In addition, it was found that the most effective reagent formulation for the dechlorination of PCBs in controlled one-phase reactions and model substrates, was <u>not</u> the most effective reagent for PCBs in soil, specifically because of its extreme sensitivity to water. The reagents described in this report are much less sensitive to deactivation with water.

LABORATORY EXPERIMENTS USING LABORATORY-CONTAMINATED SOILS

The next phase of experiments performed in this study show that a soil freshly contaminated with 1000 ppm of Aroclor 1260 can be decontaminated (to below 50 ppm PCBs) in only a few days with a direct application of KPEG 350-1 (see section 5). Particularly encouraging is the fact that this reagent can be used on soil containing some water and organics, and that it continues to react after several days in open air.

LABORATORY EXPERIMENTS WITH PCB-CONTAMINATED SOIL FROM A PHILADELPHIA, PA SPILL SITE

The next phase of testing involved a laboratory scale treatment of soil obtained from the site of an actual PCB spill. The soil used in this series of experiments was of much smaller average particle size than the soil contaminated in the laboratory in previous tests. Also in this case the PCBs had remained in contact with the soil for years. Nevertheless, the PCBs extracted from untreated soil exhibited near-perfect chromatographic profiles for Aroclor 1260.

A number of conclusions can be drawn from the series of experiments conducted under carefully controlled standardized laboratory conditions:

1. Application of reagent to wet soil is not effective in reducing the concentration of PCB's in this particular soil. The water present in a typical reaction sample greatly dilutes the reagent. Air drying of the soil is necessary prior to treatment.
2. Increased temperature, is as expected, more effective in reducing PCB concentration in soils.
3. Increased temperature also eases mixing of reagent and soil; this should aid the continued reduction of PCB in soil over time.
4. An increase in reaction time shows a continued decrease in the concentration of PCBs in the soil, particularly of the more active components.
5. A greater reagent to soil ratio has shown the best results in these experiments to date. This result is likely due in part to increased contact of reagent with PCB's. This effect can perhaps be duplicated by a better method of mixing. In addition, increased reagent to soil ratio means less soil water contamination in the reagent. This should also increase the rate of dechlorination.
6. The syringe application method, which minimizes the amount of atomospheric water coming in contact with the reagent is sufficient; no additional advantage is realized by applying the reagent to the soil under nitrogen.
7. Kerosene added to the soil as a solvent pretreatment is more effective in realizing dechlorination than toluene, or no solvent at low reaction temperatures but not significantly more effective than no solvent pretreatment when reactions are conducted at higher temperatures.
8. The reagent diluted with kerosene or toluene prior to application to the soil is not as effective in dechlorinating the PCBs as the reagent alone applied to the soil.
9. When using KPEG-350-1 reagent in order to obtain results comparable to those using KPEG-350; at least 67% more reagent must be applied to the soil.

ON-SITE TREATMENT OF PCB-CONTAMINATED SOIL

The first completed experiment in which the application of reagent to contaminated soil was carried out on-site by FRC personnel in Buffalo, NY in August 1983. This experiment produced inconclusive results in complete contrast to those obtained under laboratory-controlled conditions using the same soil.

The only known major problems which have adversely affected the results of this initial field study involve the inhibiting effect of water on the chemical degradation rate. Subsequent laboratory tests demonstrated simple techniques that may be used to minimize the adverse effects of water on the rate of decontamination.

The results of the more recent, systematic laboratory investigation are much more encouraging than the preliminary on-site test. The level of PCBs in contaminated soil can be reduced from approximately 1000 ppm (highly contaminated) to below 50 ppm by direct chemical treatment under relatively mild conditions. This suggests that the direct on-site chemical treatment of PCB-contaminated soil is promising as a process. There is, of course, considerable work that remains to be done toward the development of a fieldable process, particularly with respect to minimizing the inhibiting effect of water and optimizing treatment conditions for soil decontamination.

SECTION 3
RECOMMENDATIONS

Additional areas in which investigation should continue are outlined below:

1. Reaction products of NaPEG treatment of PCBs in soil.

   Information on mechanisms and products of the reaction of NaPEG Reagents with PCBs was obtained in a previous study. A report of this work appears in the background section of a proposal entitled "Chemically Detoxify Soil" (FRC Proposal No. 22848-G-Revised), submitted to EPA-IERL on October 17, 1983. Additional information must be obtained, however, particularly from real soil systems using currently employed treatment conditions. This information is of primary toxicological interest.

2. Optimization and development of a fieldable process.

   The work described in this study is definitely proceeding in the direction of improving the extent of soil decontamination. Considerable information has been obtained as to what steps must be taken to further improve the process, and to make it economically feasible. Future work must concentrate on large scale field tests in order to answer engineering questions which arise in the development of a fieldable process. Immediate areas which require investigation, and which may demonstrate considerable improvements in laboratory scale, include soil heating, solvent pretreatment of soil, and reagent additives (e.g., surfactants and wetting agents) which may allow greater contact of reagent to soil particles.

3. Alternative Processes

   Alternative methods of applying the chemical destruction of PCBs to contaminated soil and other spill situation show promise. In particular, solvent extraction of the contaminant from the soil followed by off-site chemical treatment should be more fully investigated as an alternative to direct on-site treatment, should the latter prove economically unfeasible. Recycling of the reagent, for example, should be much easier in an off-site process.

4. Environmental Impact

   In addition to toxicological questions which must be answered chemically (by determination of reaction products), and biologically (by conducting toxicity and bioaccumulation tests of treated soils), other environmental impacts of an on-site treatment must be assessed. In particular the fate of the excess reagent must be known and/or controlled. Also the question of whether the soil may be reused after treatment must be answered.

SECTION 4
EXPERIMENTAL PROCEDURES

NaPEG Reagents for laboratory experiments were prepared in FRC's laboratory. The reagents of their various compositions are described below. One of these reagents (KPEG 400-1) was used for the field test conducted at the Bengart and Memel site in Buffalo, NY.

Soils treated in the laboratory were prepared and/or pre-treated as described in section 5. The reagent was then applied to the soil as described below. The soil was analyzed for unreacted PCBs. Sample preparation methods employed in this study are described below.

Gas chromatography with electron-capture detection (GC-EC) was used for the quantitative determination of PCBs in soils. Aroclor PCB mixtures were used as standards. Treated and untreated soils were analyzed for PCBs. The concentration of PCBs was expressed as parts-per-million (ppm) (w/w) based on the weight of extracted, dried soil.

All analyses were performed in duplicate. In most cases experiments were performed in duplicate.

PREPARATION AND NOMENCLATURE OF THE NaPEG^{tm} REAGENTS

All formulations of FRC's Reagent are referred to as "NaPEG Reagents", including those containing potassium. Specific reagents, such as "KPEG 350-1", retain the proper alkali metal nomenclature, whereas "NaPEG Reagent" is a general term that is used to define the class of reagents. This terminology is retained, even for potassium-based reagents to avoid confusion with previous reports. The preparation of the specific reagents is as follows:

KPEG 350: Poly(ethylene glycol monomethyl ether), average molecular weight 350 (PEGM 350) was reacted with an equimolar amount of potassium metal under nitrogen. The temperature of the reaction was maintained slightly above the melting point of potassium. The greenish amber, relatively nonviscous liquid reagent was cooled to room temperature and stored under nitrogen until needed.

The reagent is composed primarily of the potassium salt of PEGM 350 in which the potassium ion is complexed by the polyglycol chain.

KPEG 350-1: KOH pellets were dissolved in an equimolar amount of PEGM 350 under nitrogen at approximately 100°C. The amber, viscous reagent was stored under nitrogen until needed. The reagent contains primarily a KOH/PEGM complex in equilibrium with the potassium salt of PEGM, which is the reactive species. The reagent contains some precipitate (mainly KOH) at room temperature.

KPEG 400-1: Prepared in the same manner as KPEG 350-1, but using polyethylene glycol, average molecular weight 400 (PEG 400) instead of PEGM 350. This reagent is also an amber viscous liquid which is primarily a KOH/PEG complex in equilibrium with the monopotassium, and possibly dipotassium salts of PEG 400.

NaPEG 400-N: PEG 400 was reacted wih molten sodium metal at approximately 100°C under nitrogen. As with all reactions involving alkali metal reactants, the metal was added slowly, in small portions. When 1.1 moles of sodium was consumed per mole of PEG 400, the reaction slowed considerably and was terminated. The viscous amber liquid was cooled and stored in the same manner as the other reagents.

This reagent consists primarily of mono- and disodium salts of PEG 400 in which the sodium ion is complexed by the PEG chain.

NaPEG 350-1: Prepared in the same manner as KPEG 350-1, but with NaOH in place of KOH. The reagent is the sodium analog of KPEG 350-1, and has similar physical properties.

SOIL TREATMENT STUDIES

Laboratory Treatment Procedure for PCB-Spiked Soils

The reagent was warmed to approximately 100° before being added to 500 g samples of contaminated soils. The treated soil samples were mixed thoroughly for one minute, then let stand. In all cases except one the reactions were conducted entirely in open air. In that experiment, the reagent and soil were mixed in a nitrogen atmosphere and then the mixture was let stand in open air for the duration of the reaction. Each NaPEG-treated soil sample was kept in an open jar so that the depth of soil was approximately 3 inches.

Laboratory Treatment Procedure for Buffalo, NY Soil - Preliminary Indoor Tests

Soil samples from test area I (0-6 inches and 6-12 inches below the surface), and test area II (0-6 inches and 6-12 inches) were combined. Approximately equal weights of each of the four samples were mixed thoroughly and divided into two equal portions. To one portion was added 10 weight percent of KPEG-350. The reagent was added and mixed thoroughly in the soil in an open air indoor environment. The treated soil was let stand at room temperature for 37 days, after which time two aliquots of each sample were analyzed for residual PCBs. The other portion of "combined soil" was similary treated with KPEG-350-1, a reagent more like that used in the field tests in that it was prepared with KOH.

Standardized Laboratory Treatment Procedure for PCB-Contaminated Soil

Soil was air dried for 3 days in a hood prior to use, or wet soil was used directly. 100 g of soil was weighed into a 4 oz. screw-cap jar, the soil was equilibrated in an oven at the appropriate reaction temperature. The reagent was added by inserting a syringe filled with reagent into the soil; the soil and reagent were then mixed thoroughly for 1-5 minutes. The jars were returned to the oven, then analyzed at the appropriate time. Reaction temperatures, reagent-to-soil ratos and methods of mixing were varied in the experimental program.

Field Treatment Procedure - First Test with Bengart and Memel Soil, Buffalo, NY

On 22 August 1983, approximately 13 gallons of KPEG-400-1 was poured onto test area II at the Bengart & Memel, Buffalo, NY site. The reagent was thoroughly mixed with the soil. A shovel was used to assure adequate mixing, which took approximately 1 hour of manual agitation of the 4 foot by 8 foot by 6 inch (deep) plot.

Soil samples taken from the test area on the following dates were received at FRC and analyzed within 2 weeks of sampling.

1 September 1983 (10 days after treatment)

12 September 1983 (21 days after treatment)

14 October 1983 (53 days after treatment)

17 May 1984 (269 days after treatment).

The sets each consisted of a composite soil sample containing portions of treated soil taken from various locations within the test area, and an untreated "control" sample from an adjacent test area. No control sample was taken on the final sampling date.

SAMPLE PREPARATION METHODS

Modified Soxhlet Extraction of PCBs from Soil

Ten gram aliquots of soil were placed in a round bottom flask. In chemically treated soil samples, the reaction was quenched prior to extraction by adding approximately 2 grams of water to the soil aliquot. This prevents the heat from the condensing solvent from accelerating dechlorination reactions during the extraction step. The aliquots were then extracted with 1:1 (v/v) acetone/hexane in a soxhlet extractor. The post-extraction workup required modification from the EPA method[3] because the presence of excess reagent in treated samples hinders the transfer of unreacted PCBs from the extract into the hexanes phase. The workup was modified as follows:

a) 150 ml of solvent was used for Soxhlet extraction

b) Extract was added to 250 ml of deionized water in a 500-ml separatory funnel, to which an additional 75 ml of acetone was added (to prevent emulsification).

c) The organic layer was separated. Four 30 ml portions of hexane were then used to extract the aqueous layer.

d) The organic portions were combined and placed a 200 ml volumetric flask. Hexane was added to fill to volume.

e) Appropriate dilutions were made to provide a hexane solution with PCB concentration in the range of 1 mg/l.

f) 10 ml of the solution was stirred vigorously with 5 ml of concentrated H_2SO_4 for 3-5 minutes.

g) 5 ul of the H_2SO_4-treated solution was injected into the gas chromatograph. PCB concentration was calculated by the method described under "Analytical Method".

h) The extracted soil was dried and weighed.

Shaker Extraction of PCBs from Soil

Ten gram aliquots of soil were removed from the reaction vessel and placed in a 4 oz. jar with teflon lined screw cap lid. 50 ml solvent (1:1 mixture acetone:hexane) was added, then the jar was agitated for 3 hrs. on a wrist action shaker. The soil was allowed to settle and the liquid decanted into a 250 ml erlenmeyer flask. The soil was rinsed 3 times with 25 ml solvent. All extracts were combined. The soil was weighed after it had dried.

The combined extract was added to 250 ml deionized H_2O in a 500 ml separatory funnel to which was added an additonal 75 ml acetone. The organic layer was separated. Four 30 ml portions of hexanes were used to extract the aqueous layer. The organic portions were combined and placed in a 200 ml volumetric flask; hexane was added to fill to volume. After Appropriate dilutions, 10 ml of the solution was stirred vigorously with 5 ml concentrated H_2SO_4. The hexane solution was analyzed for PCBs by the GC-EC method described below.

ANALYTICAL METHOD

Unreacted PCBs extracted from soil samples were quantitated by gas chromatography with electron capture detection (GC-EC). Aroclors 1242, 1254 and 1260, 1 mg/liter in hexane, were used as standards. 5 ul of standards, and samples diluted with hexane to approximately 1 mg/liter PCBs, were injected for each analysis. The method of Webb and McCall[4] was used to quantitate PCBs by individual peaks, using pre-determined response factors for each peak. When sample chromatograms closely resembled those of one of the above Aroclors, an approximation was made by comparing the total (summed) peak area of the sample to that of the standard.

The concentration of PCBs is calculated as follows:

$$C_{(ppm)} = \frac{M^S \times V^X \times R^X}{v^X \times W^X \times R^S}$$

where

M^S = mass of standard injected, in nanograms

V^X = total volume of sample, times dilution factors, in milliliters

R^X, R^S = chromatogram response of sample and standard peaks, respectively, in peak area units.

V^X = volume of sample solution injected, in microliters

W^X = weight of the sample matrix (extracted, dried soil), in grams.

In most series of tests, PCB concentration was also calculated for one or two individual chromatographic peaks. "C_1" is defined as the concentration, in ppm, determined for components with relative retention[3] of 117 and 125 by using the combined area of the two peaks in the above equation. "C_2" is defined as the concentration, in ppm, determined for components with relative retention time[3] of 280.

SECTION 5
LABORATORY STUDIES

Experiments conducted at the onset of this study were performed primarily to determine the optimum reagent composition for soil studies. Subsequent experimentation focused on the examination of several of the most reactive reagents and other reaction variables on PCB-spiked soils. Data obtained in these experiments are detailed in previous progress reports.

Experiments using soils spiked with PCBs were resumed after a completion of tests using model substrates. Experimental conditions and procedures were greatly revised in light of earlier results. This second series of tests with spiked soil is described in detail in this section.

Two series of laboratory tests were then conducted using actual PCB-contaminated soil from the Buffalo, NY site. The first tests demonstrated the effect of NaPEG treatment on contaminated soil obtained from the site before field treatment. Later tests examined the effects of adding additional reagent to soil obtained from the field-treated plot nine months after the on-site application of the reagent.

Laboratory tests conducted during the second year of this project centered mainly on the treatment of PCB-contaminated soil obtained from the Brown Boveri Inc. site in Philadelphia, PA. The effects of temperature, solvents, mixing conditions and pretreatment methods were examined in greater detail in this series of tests. The testing was limited to two reagent compositions: KPEG 350, the most effective reagent for PCB-contaminated soils, and KPEG 350-1, a less effective, but lower cost alternative.

TREATMENT OF LABORATORY-CONTAMINATED SOILS

This phase of testing was directed primarily toward demonstrating that the concentration of PCBs in soil can be reduced to below 50 ppm by direct addition of the NaPEG reagent under ambient conditions typical of an in-situ treatment of a spill. In these laboratory experiments the reagent was preheated and applied to the contaminated soil in an indoor environment at room temperature. Multistep applications were employed and the reagent was heated prior to application to the soil.

A coarse, sandy soil was obtained from a non-contaminated site in New Jersey. The soil was spiked to a level of approximately 1000 ppm with Aroclor 1260. The spiked soil was extracted to assure quantitative recovery. The acetone/hexane soxhlet extraction procedure described in section 4 was used.

The reagent was added to the soil as described in section 4 (see "Laboratory Treatment Procedure for PCB-Spiked Soils"). After predetermined reaction times, ten gram aliquots of the soil were removed and analyzed for PCBs, using the procedure described above for untreated soils. Additional portions of reagent were applied to the soil in most of these experiments, at various time intervals, up to 6 months in some cases. Results of analyses of remaining PCBs in the soils are presented in Tables 1 to 7. Analyses of two aliquots of the same reaction were performed in most cases.

TABLE 1. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH NaPEG 400-N

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0	254-34-1A	Unspiked Soil (Blank)	0.64	1260
0	254-34-1B	Unspiked Soil (Blank)	0.58	1260
0	254-34-2A	Spiked Soil[b]	1349	1260
0	254-34-2B	Spiked Soil	1238	1260
0		50g Rgt. Applied	-	-
1	254-36-2A	Soil Analyzed	515	1260
1	254-36-1A	Soil Analyzed	492	1260
5	254-40-1	Soil Analyzed	410	1260
5	254-40-2	Soil Analyzed	535	1260
5		51g Rgt. Applied	-	-
6	254-41-1	Soil Analyzed	399	1254
6	254-41-2	Soil Analyzed	408	1254
11		100g Rg. Applied	-	-
13	254-42-1	Soil Analyzed	399	1254
13	254-42-2	Soil Analyzed	426	1254

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil spiked with approximately 1000 ppm Aroclor 1260.

TABLE 2. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH KPEG 350-1

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0	254-37-1	Spiked Soil[b]	951	1260
0		51g Rgt. Applied	-	-
1	254-38-2A	Soil Analyzed	722	1260
1	254-38-2B	Soil Analyzed	713	1260
2		56g Rgt. Applied		
3	254-38-2C	Soil Analyzed	316	1254
3	254-38-2D	Soil Analyzed	320	1254
7		100g Rgt. Applied	-	-
9	254-39-1	Soil Analyzed	124	1254
9	254-39-2	Soil Analyzed	110	1254
14	254-39-3	Soil Analyzed	110	1254
14	254-39-4	Soil Analyzed	67	1254
28	254-39-5	Soil Analyzed	40	1254
28	254-39-6	Soil Analyzed	48	1254

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil spiked with approximately 1000 ppm Aroclor 1260.

TABLE 3. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH KPEG 350-1

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0		51g Rgt. Applied	-	-
0 (1 hr)	254-45-1	Soil Analyzed, then 50g Rgt. Applied	863	1260
0 (2 hr)	254-45-2	Soil Analyzed, then 52g Rgt. Applied	556	1254
0 (3 hr)	254-45-3	Soil Analyzed, then 50g Rgt. Applied	282	1254
0 (4 hr)	254-45-4	Soil Analyzed, then 50g Rgt. Applied	146	1254
1 (22 hr)	254-45-5	Soil Analyzed	42[c]	1254
1	254-45-6	Soil Analyzed	101	1254
5	254-45-7	Soil Analyzed	30	1254
5	254-45-8	Soil Analyzed	27	1254
12	254-45-9	Soil Analyzed	25[c]	1254
12	254-45-10	Soil Analyzed	49	1254
176	254-60-1	Soil Analyzed	49	d
176	245-60-2	Soil Analyzed	53	d

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil spiked with approximately 1000 ppm Aroclor 1260.

c Lower values result from aliquots taken from top layer of soil. The reagent settles, apparently holidng on to excess PCBs.

d PCBs were quantitated by comparing individual peaks to those of Aroclor standards. See section 4.

TABLE 4. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH KPEG 350-1 (APPLIED UNDER N_2)[b]

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0		52g Rgt. Applied	-	-
1	254-48-1	Soil Analyzed	428	1254
1	254-48-2	Soil Analyzed	406	1254
5	254-48-3	Soil Analyzed	366	1254
5	254-48-4	Soil Analyzed	336	1254
176	254-60-3	Soil Analyzed	298	c
176	254-60-4	Soil Analyzed	297	c

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil spiked with approximately 1000 ppm Aroclor 1260.

c PCBs were quantitated by comparing individual peaks to those of Aroclor standards. See section 4.

TABLE 5. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH NaPEG 350-1[b]

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0		52g Rgt. Applied	-	-
1	254-50-1	Soil Analyzed	688	1260
1	254-50-2	Soil Analyzed	667	1260
5	254-50-3	Soil Analyzed	647	1260
5	254-50-4	Soil Analyzed	624	1260
6		55g Rgt. Applied	-	-
7	254-50-5	Soil Analyzed	466	1254
7	254-50-6	Soil Analyzed	504	1254
12	254-50-7	Soil Analyzed	395	1254
12	254-50-8	Soil Analyzed	365	1254
12		100g Rgt. Applied	-	-
13	254-50-9	Soil Analyzed	202	1254
13	254-50-10	Soil Analyzed	245	1254
176	254-60-5	Soil Analyzed	67	c
176	254-60-6	Soil Analyzed	80	c

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil Spiked with approximately 1000 ppm Aroclor 1260.

c PCBs were quantitated by comparing individual peaks to those of Aroclor standards. See section 4.

TABLE 6. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH PEG 350 FOLLOWED BY KPEG 350-1[b]

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0		52g Rgt. Applied	-	-
1	254-53-1	Soil Analyzed	724	1260
1	254-53-2	Soil Analyzed	535	1260
7	254-53-3	Soil Analyzed	452	1260
7	254-53-4	Soil Analyzed	421	1260

TABLE 7. TREATMENT OF AROCLOR 1260 - SPIKED SOIL WITH KPEG 350-1[b]

Day	Sample No.	Description	[PCB][a], ppm	Analyzed as Aroclor No.[a]
0		100g Rgt. Applied	-	-
1	254-57-1	Soil Analyzed	232	1254
1	254-57-2	Soil Analyzed	217	1254
164	254-60-7	Soil Analyzed	136	c
164	254-60-8	Soil Analyzed	118	c

a PCBs were quantitated by comparing total chromatogram peak area to that of the listed Aroclor standard.

b Soil spiked with approximately 1000 ppm Aroclor 1260.

c PCBs were quantitated by comparing individual peaks to those of Aroclor standards. See section 4.

LABORATORY TREATMENT OF PCB-CONTAMINATED SOIL FROM A BUFFALO, NY SPILL SITE

Analysis of Soil Samples from Various Locations at the Bengart & Memel Site - Before Treatment

Ten soil samples from a Buffalo, NY were received in July 1983. Soil samples weighing approximately 50-100 grams were obtained from various depths at the two test plots and the "control" area. Two 10 gram aliquots of each soil sample were extracted by the acetone/hexane Soxhlet extraction procedure described in section 4, and analyzed for PCBs by GC-EC. In each case the chromatogram of the extracted PCBs resembled that of Aroclor 1260, but quantitation nevertheless was done by comparing individual peaks to 3 Aroclor standards (see section 4). The total concentration of PCBs are expressed as ppm based on the weight of the extracted, dried soil. The concentration of PCBs arising from several selected chromatogram peaks are listed for comparison in samples of soil taken from uppermost layers. Results are listed in Table 8.

TABLE 8. RESULTS OF PCB ANALYSES OF BUFFALO, NY SOIL BEFORE FIELD TREATMENT

Ref. No.	Test Area	Total Soil Depth	[PCBs][a] ppm	C^a_{125}	C^a_2
244-28-1, 2	Control	12"-18"	45.0 46.4		
244-28-3, 4	Control	18"-24"	27.0 28.0		
244-28-9, 10	I	0"-6"	60.8 63.1	6.1 5.8	5.3 -
244-28-5, 6	I	6"-12"	68.0 83.5	4.7 4.6	- -
244-28-11, 12	I	12"-18"	38.9 -		
244-28-7, 8	I	18"-24"	16.3 15.8		
244-28-13, 14	II	0"-6"	127.0 138.0	12.6 14.4	19.0 22.1
244-28-15, 16	II	6"-12"	109.0 127.0	8.7 12.1	12.3 17.0
244-28-17, 18	II	12"-18"	30.0 21.2		
244-28-19, 20	II	18"-24"	39.3 25.6		

a C_{125} is defined as the concentration, in ppm, found in peak 125. It is roughly 20% lower than C_1, which along with C_2 is used to follow the reduction in conc. of selected PCB components. C_1 and C_2 are defined in secion 4 under "Analytical Method".

b Analyses were performed in duplicate, e.g., 244-28-2 is duplicate of 244-28-1.

Analysis of Control Samples by Alternate Modified Extraction Methods

The results of PCB analyses of Buffalo, NY soil appear to suggest that the extraction and/or workup procedure used for reagent treated soils is ineffective for untreated soils. In an attempt to use the same soil extraction/sample preparation workup procedure for treated and untreated soils, several additional modifications to the method were made. Specifically, improvements in the recovery of PCBs (from the soil to the sample injected into the GC) were sought for the untreated, PCB-contaminated soils from the site. The Soxhlet extraction procedure described in section 4 was effective for untreated soils which were spiked with Aroclor 1260 in our laboratory, but apparently not for soil from the site. The unmodified U.S. EPA analytical methods[3,5] were also examined for untreated Buffalo, NY soil, but were found to be even less effective than the modified method.

Alternate modifications to the Soxhlet extraction procedures were as follows:

Control soil taken on 12 September 1983 was divided into two portions. PEG 350 monomethyl ether, 10 weight percent, was thoroughly mixed into one portion. After 3 days the soil was Soxhlet extracted as described previously, and PCBs in the extract were determined by GC-EC. The second portion of the soil was treated with 50% aqueous KOH in a smiliar manner 3 days prior to extraction. Results of PCB analyses are listed in Table 9. Each analysis was run in duplicate.

TABLE 9. RESULTS OF ANALYSES OF CONTROL SAMPLES BY ALTERNATE MODIFIED EXTRACTION METHODS

Ref. No.[b]	Description	Total[PCB]ppm[b]	C_1[a]	C_2[a]
244-40-1, 2	Control, 21 days outdoors	132	17.5	9.3
	& PEG 350	163	21.1	11.6
244-40-3, 4	Control, 21 days outdoors	114	15.1	8.2
	& 50% KOH	138	18.1	9.7

a C_1 and C_2 are defined in section 4 under "Analytical Method".

b Experiments were performed in duplicate.

Preliminary Laboratory (Indoor) Treatment of PCB-Contaminated Soil from the Buffalo, NY Site

A series of laboratory experiments using PCB-contaminated soil from the site were conducted concurrently with the field tests. The two most promising NaPEG Reagents were investigated, which were expected to be more effective than the reagent formulation used in the field tests.

The soil samples were obtained, prepared and treated as described in section 4 (see "Laboratory Treatment Procedure for Buffalo, NY Soil - Preliminary Indoor Tests"). Duplicate 10 gram aliquots were analyzed af - 37 days for residual PCBs by the Soxhlet extraction method described in section 4. Quantitation was done by comparing individual peaks of the sample chromatogram to Aroclor standards (see section 4). Results are listed in table 10.

TABLE 10. RESULTS OF INDOOR TREATMENT OF BUFFALO, NY SOIL WITH VARIOUS NaPEG REAGENTS

Ref. No.[b]	Description	Total[PCB] ppm	C_1[a]	C_2[a]
	Combined Soil Sample	Approx 101[c]		11.7[c]
249-39-A1, A2	Combined Soil &	33.6	4.6	2.9
	KPEG-350, 37 days	52.3	6.3	4.1
249-39-C1, C2	Combined Soil &	114	15.5	10.9
	KPEG-350-1, 37 days	94	13.1	8.6

a C_1 and C_2 are defined in section 4 under "Analytical Method".

b Experiments were performed in duplicate.

c Results calculated by averaging Table 1 values.

Additional Indoor Treatment of Soil from the Field-Treated Plot at the Buffalo, NY Site

A composite sample of field-treated soil was taken from the Buffalo, NY site on May 17, 1984 and brought to FRC. The soil was analyzed and then subjected to further chemical treatment in the laboratory. The soil was air dried, homogenized, pulverized with mortar and pestle, and sifted through 1/16-inch screen. The pH of the soil prior to reagent addition was measured at 9.0. The standardized laboratory treatment procedure, described in section 4 was used for this series of tests. Ten gram aliquots were removed after pre-determined time intervals, extracted by the "shaker" extraction method (section 4), and analyzed for PCBs. Results are listed in Table 11.

TABLE 11. RESULTS OF 80°C INDOOR TREATMEN OF BUFFALO, NY SOIL OBTAINING FROM THE FIELD TREATED PLOT

Ref No.	Reagent	Soil to Reagent Ratio (w/w)	Time to Analysis (days)	Total PCB (ppm)[b]	C_1[a]	C_2[a]
249-66-1	KPEG 350-1	6.7:1	1	343	58.4	30.6
	"	6.7:1	5	95	14.7	7.4
	"	6.7:1	18	192	30.8	11.9
249-66-2	"	6.7:1	1	450	67.8	41.6
	"	6.7:1	5	211	33.4	13.0
	"	6.7:1	18	258	37.8	19.6
249-66-3	KPEG 350	10:1	1	306	46.4	41.6
	"	10:1	5	172	28.2	9.1
	"	10:1	18	204	34.2	10.1
249-66-4	"	10:1	1	308	47.6	31.4
	"	10:1	5	256	41.2	16.2
	"	10:1	18	229	37.6	14.3
249-66-5	NONE	-	1	598	88.3	67.7
	"	-	5	315	45.5	31.3
	"	-	18	326	42.2	39.9
249-66-6	"	-	1	452	66.8	67.7
	"	-	5	334	48.0	33.6
	"	-	18	-	-	-

a C_1 and C_2 are defined in section 4 under "Analytical Method".

b Experiments were performed in duplicate, e.g. expt. 249-66-2 is duplicate of expt. 249-66-1.

LABORATORY TREATMENT OF PCB-CONTAMINATED SOIL FROM A PHILADELPHIA, PA SPILL SITE

Baseline and Solvent Studies

This and following series of experiments involving off-site chemical treatment of PCB-contaminated soil was undertaken with the ultimate objective of improving the treatment method of PCB destruction in soil contaminated by an actual spill using NaPEG^{tm} reagents. Previous studies (see the section entitled "Treatment of Laboratory Contaminated Soil") showed that soil freshly contaminated with 1000 ppm Aroclor 1260 can be decontaminated to below 50 ppm PCB's by direct application of NaPEG^{tm} reagents. The effort in these studies was to provide the information needed to improve the extent of soil decontamination using actual environmental samples and decrease the amount of reagent necessary for soil decontamination.

Two 5 gallon cans of soil and stone were received from Brown-Boveri, Inc., Philadelphia, PA. In order to eliminate variations in experimental results from the different cans, the two cans were combined, thoroughly mixed, then passed through a 3/8 inch mesh screen to eliminate large stones and materials. The soil was extracted by the "shaker" method (section 4), and analyzed to contain 14.5% H_2O, and 1150 ppm PCB as Aroclor 1260. It should be noted that the soil had been contaminated with PCBs for at least three years, but the recovered components were still in the correct proportions expected for Aroclor 1260. Successive extractions produced no significant amount of additional PCBs.

A series of experiments was conducted with variations in temperature, water content, reagent application and reagent ratio. The purpose of these experiments is to find the best combination of these variables which is potentially a practical extension to field study application. All experiments were conducted in duplicate and KPEG 350 was used. Samples were treated by the standardized method described in section 4. After various reaction times, aliquots were removed, extracted by the "shaker" method, (section 4) and analyzed for PCBs. Results are listed in tables 12 and 13.

Table 12. Results of Indoor Treatment of Philadelphia, PA Soil - Baseline Studies

Expt[b]	Pre-Treatment[c]	Soil:Rgt Ratio w/w	Temp (°C)	Rxn. Time (days)	Appl. of Rgt.	[PCB] (ppm)	C_1[a]	C_2[a]
1	none	none	(untreated soil)		-	1165.3	168.2	80.1
2	none	10:1	40	1	under N_2	1115	159.5	83.2
2a	"	"	"	"	"	d	d	d
3	"	"	65	"	"	1271	182.7	94.7
3a	"	"	"	"	"	950	137.9	67.7
4	"	"	80	"	"	989	145.5	73.2
	"	"	"	3	"	1052	153.3	75.7
4a	"	"	"	1	"	1130	168.1	84.6
5	A	5:1	"	1	"	98	4.6	ND
	"	"	"	3	"	79	5.4	ND
5a	"	"	"	1	"	581	25.6	14.0
	"	"	"	3	"	346	61.6	5.5
6	"	10:1	"	1	"	765	122.9	39.3
	"	"	"	2	"	775	131.3	37.9
	"	"	"	3	"	147	23.6	6.9
6a	"	"	"	1	"	1238	195.4	62.1
	"	"	"	2	"	805	129.2	38.1
	b	"	"	3	"	233	38.5	9.4
7	b	10:1	40	1	under N_2	811	-	31.0
	"	"	"	5	"	917	164.2	24.9
7a	"	"	"	1	"	690	123.5	22.4
	"	"	"	5	"	607	105.7	15.5
8	"	"	"	1	in air	1073	164.8	59.9
	"	"	"	2	"	1008	154.1	42.7
	"	"	"	3	"	497	86.1	20.8
8a	"	"	"	1	"	1076	172.8	64.8
	"	"	"	2	"	861	154.2	30.1
	"	"	"	3	"	629	106.9	25.8
9	B	"	20	1	"	734	115.6	42.4
	"	"	"	2	"	780	117.5	46.4
	"	"	"	3	"	662	101.3	41.4
9a	"	"	"	1	"	892	137.8	50.5

a C_1 and C_2 are defined in section 4 under "Analytical Method".
b Reactions were performed in duplicate, e.g. expt. 1a is duplicate of expt. 1
c See Appendix C for descriptions of soil pre-treatment steps
d Analytical data discarded.
ND None detected

Table 13. Results of Indoor Treatment of Philadelphia, PA Soil

Expt[b]	Pre-Treatment[c]	Soil:Rgt Ratio w/w	Temp (°C)	Rxn. Time (days)	Appl. of Rgt.	[PCB] (ppm)	C_1[a]	C_2[a]
10	C	10:1	22	1	in air	707	121.1	35.7
	"	"	"	5	shaken for	439	83.4	13.2
	"	"	"	16	15 minutes	379	58.0	12.3
10a	"	"	"	1	"	608	90.0	22.0
	"	"	"	5		226	61.1	6.8
	"	"	"	16		279	55.8	8.6
A-10	"	"	80	1	"	729	203.5	28.2
	"	"	"	5		284	43.8	12.2
A-10a	"	"	"	1		1007	281.5	34.6
	"	"	"	5		327	54.4	13.3
B-10	"	5:1	"	1	"	194	65.8	ND
	"	"	"	5		140	50.6	ND
B-10a	"	"	"	1		147	23.0	2.5
	"	"	"	5		163	29.7	1.9
11	D	10:1	"	1	"	663	115.0	42.2
	"	"	"	5		574	100.1	29.1
	"	"	"	16		360	66.8	20.2
11a	"	"	"	1	"	841	123.1	46.4
	"	"	"	5	"	480	87.3	24.2
	"	"	"	16	"	391	71.4	20.2
12	E	"	65	1	rgt. mixed	1122	160.7	60.1
	"	"	"	5	1:1 (w/w)	577	108.0	25.5
12a	"	"	"	1	w/kerosene	1420	200.1	65.1
	"	"	"	5	under N , then applied in air	708	127.0	30.9
13	"	"	"	1	rgt. mixed	1212	172.5	79.6
	"	"	"	5	1:1 (w/w)	463	84.1	26.5
13a	"	"	"	1	w/toluene	1271	177.9	85.6
	"	"	"	5	under N , then applied in air	593	113.2	38.7

a C_1 and C_2 are defined in section 4 under "Analytical Method".
b Reactions were performed in duplicate, e.g. expt. 1a is duplicate of expt. 1
c See Appendix C for descriptions of soil pre-treatment steps
ND None detected

Examination of KPEG 350-1 Reagent with Soil from the Philadelphia, PA Site

KPEG 350-1, the reagent prepared using KOH was re-investigated in the chemical treatment experiments using the soil from the contaminated soil. KPEG 350-1 may be much less expensive to manufacture on a large scale than KPEG 350. Although KPEG 350-1 is known to be less effective than KPEG 350, it may be useful in field applications as a lower cost alternative to the more reactive reagent. The next series of experiments examined the treatment of the PCB-contaminated soil with KPEG 350-1 under various controlled conditions.

All experiments were performed in duplicate under standardized treatment conditions described in this section for the baseline and solvent studies. Experimental and analytical procedures are presented in sections 4. Sample preparation and analysis was conducted in a similar manner.

One set of experiments was conducted using KPEG 350-1 prepared as described in section 4. The results of these tests are listed in table 14. Two additional experiments used an alternate KPEG 350-1 treatment in which the reagent was generated in-situ by adding the appropriate amounts of KOH and PEGM 350 to the soil. The KOH was pulverized under nitrogen immediately before use. Dissolution of the KOH occurred during the vigorous mixing that followed the reagent application. Results of tests using the reagent prepared in-situ are listed in table 15.

Table 14. Results of Indoor Treatment of Philadelphia, PA Soil with KPEG 350-1

Expt[b]	Pre-treatment[c]	Soil to Reagent Ratio w/w	Temp. °C	Rxn Time (days)	PCB (ppm)	C_1[a]	C_2[a]
14	F	6.7:1	80	1	798	125	48.4
	"	"	"	5	777	129	42.7
	"	"	"	14	526	94.3	30.2
14a	"	"	80	1	662	105.1	38.2
	"	"	"	5	782	116.1	42.6
	"	"	"	14	543	94.4	33.7
15	G	6.7:1	80	1	280	23.8	1.3
	"	2:1	"	5	242	34.1	0.9
	"	2:1	"	14	28	0.3	0.1
15a	"	6.7:1	80	1	212	27.0	0.9
	"	2:1	"	5	180	23.3	0.9
	"	2:1	"	14	113	6.6	0.1
16	F	4:1	80	1	539	93.7	9.3
	"	"	"	5	500	81.0	ND
	"	"	"	14	392	75.0	"
16a	"	"	"	1	383	71.4	"
	"	"	"	5	444	60.6	"
	"	"	"	14	399	71.9	"
17	"	3:1	"	1	269	42.6	ND
	"	"	"	5	122	10.3	0.1
	"	"	"	14	103	7.0	0.2
17a	"	"	"	1	251	35.1	ND
	"	"	"	5	116	19.7	0.1
	"	"	"	14	164	16.2	0.2
18	H	2:1	"	1	29	2.3	ND
	"	"	"	5	12	0.6	0.1
	"	"	"	14	13	0.5	0.1
18a	"	"	"	1	38	2.6	ND
	"	"	"	5	27	1.0	0.1
	"	"	"	14	22	0.6	0.6

Table 14. Results of Indoor Treatment of Philadelphia, PA Soil with KPEG 350-1 (continued)

Expt[b]	Pre-treatment[c]	Soil to Reagent Ratio w/w	Temp. °C	Rxn Time (days)	PCB (ppm)	C_1[a]	C_2[a]
19	H	4:1	80	1	532	96.5	ND
	"	"	"	5	395	74.3	"
	"	"	"	14	306	59.3	"
19a	"	"	"	1	509	88.0	"
	"	"	"	5	489	74.7	"
	"	"	"	14	392	77.1	"
20	J	"	"	1	527	87.8	23.6
	"	"	"	5	320	48.7	7.5
	"	"	"	14	505	84.8	7.2
20a	"	"	"	1	468	79.5	16.7
	"	"	"	5	497	66.9	19.8
	"	"	"	14	397	67.1	8.1
21	K	"	"	1	245	38.9	ND
	"	"	"	5	219	30.2	ND
	"	"	"	14	212	27.7	0.3
21a	"	"	"	1	224	34.5	ND
	"	"	"	5	255	31.0	ND
	"	"	"	14	280	37.9	1.3

a C_1 and C_2 are defined in section 4 under "Analytical Method".
b Reactions were performed in duplicate, e.g. expt. 1a is duplicate of expt. 1
c See Appendix C for descriptions of soil pre-treatment steps
ND None detected

Table 15. Results of Indoor Treatment of Philadelphia, PA Soil with KPEG 350-1 Reagent Prepared In-Situ

Expt[b]	Pre-treatment[c]	Soil to Reagent Ratio w/w	Temp. °C	Rxn Time (days)	PCB (ppm)	C_1[a]	C_2[a]
22	K	4:1	80	1	310	43.4	0.8
	"	"	"	5	243	27.2	0.2
	"	"	"	14	316	82.0	ND
22a	"	"	"	1	141	10.0	0.2
	"	"	"	5	112	5.3	0.1
	"	"	"	14	130	59.4	ND
23	none	"	"	1	464	83.4	9.0
	"	"	"	5	367	62.2	9.2
	"	"	"	14	330	63.3	8.4
23a	"	"	"	1	630	110	12.3
	"	"	"	5	599	100	12.4
	"	"	"	14	451	67.1	7.2

a C_1 and C_2 are defined in section 4 under "Analytical Method".
b Reactions were performed in duplicate, e.g. expt. 1a is duplicate of expt. 1
c See Appendix C for descriptions of soil pre-treatment steps
ND None detected

Examination of Surfactants in Reagent Compositions

Several polyglycol-based surfactants were provided to us by Mr. Alan W. Schneider of Alkem Inc. Three of the surfactants were selected for initial testing in dechlorinating reagent formulations based on their molecular structure. Alnox BP-44, BP-53 and DD-15 components possessed the polyethylene glycol moiety attached to less polar aliphatic chains. These features produce a high molecular weight liquid with relatively low viscosity. Nucleophilic reagents prepared with these surfactants are likely to have the desired reactivity with chlorinated aromatics, as well as a greater compatibility with both chlorinated contaminants and soil particles.

The first series of tests (experiments 24-26) were conducted using these surfactants in place of PEGM 350 in reagents prepared in-situ with KOH. The weight ratios of KOH-to-polyglycol, and reagent-to-soil were maintained as in experiments 22 and 23.

Two additional comparison experiments were conducted using the most effective surfactant in alternate reagent formulation. Experiment 27 utilized the Alnox DD-15/KOH reagent prepared beforehand; experiment 28 was performed using a 4:1 mixture of KPEG 350 and the Alnox DD-15/KOH reagent. The results of experiments 24-28 are listed in Table 16.

Table 16. Results of Indoor Treatment of Philadelphia, PA Soil

Expt[b]	Reagent[d] Pre-treatment[c]	Soil to Reagent Ratio (w/w)	Temp. °C	Rxn Time (days)	PCB (ppm)	C_1[a]	C_2[a]
24	I,K	4:1	80	1	616	106	22
	"	"	"	5	602	188	14
	"	"	"	14	618	103	16
24a	"	"	"	1	750	123	40
	"	"	"	5	630	103	26
	"	"	"	14	663	122	10
25	II,k	"	"	1	360	71	ND
	"	"	"	5	402	77	3.5
	"	"	"	14	491	91	4.6
25a	"	"	"	1	465	78	ND
	"	"	"	5	647	118	8.4
	"	"	"	14	994	188	6.2
26	III,k	"	"	1	470	81	ND
	"	"	"	5	257	44	ND
	"	"	"	14	240	42	ND
26a	"	"	"	1	610	105	22
	"	"	"	5	563	105	15
	"	"	"	14	611	118	ND
27	IV,k	"	"	1	362	71	ND
	"	"	"	5	504	91	5.3
27a	"	"	"	1	773	128	30
	"	"	"	5	817	138	30
28	V,k	"	"	1	437	79	ND
	"	"	"	5	544	84	ND
28a	"	"	"	1	454	80	ND
	"	"	"	5	580	92	ND

a C_1 and C_2 are defined in section 4 under "Analytical Method".
b Reactions were performed in duplicate, e.g. expt. 1a is duplicate of expt. 1
c See Appendix C for descriptions of soil pre-treatment steps
d. See text for a description of the following reagents:

I. Alnox BP-44/KOH, prepared in situ (20% KOH)
II. Alnox BP-53/KOH, prepared in situ (20% KOH)
III. Alnox DD-15/KOH, prepared in situ (20% KOH)
IV. Reagent III prepared in advance
V. Reagent III (20%) mixed with KPEG 350 (80%)
ND None detected

SECTION 6
PRELIMINARY ON-SITE TESTING AT A BUFFALO, NY SPILL SITE

On August 22, 1983, the direct application of a NaPEG Reagent to the PCB-contaminated soil was made at the Bengart and Memel site in Buffalo, NY. The reagent was applied to Test Area II, a 4 foot x 8 foot x 6 inch (deep) plot of soil. Clear plastic sheets were placed 6 inches below the soil surface and on the soil surface prior to treatment. Various heavy objects were used to hold down the plastic cover. Preparation and sampling of the site was made by personnel from Malcolm Pirnie, Inc. Experimental details of the chemical treatment and sampling are described in section 2.2.

Composite soil samples were obtained from the plot periodically after treatment. The samples were obtained by removing soil from each of six separate locations in the chemically treated plot. Care was taken to assure that the soil was uniformly removed from all depths down to the lower plastic sheet. Control samples were obtained from an area adjacent to Test Area II that was not subjected to chemical treatment.

Duplicate, 10 gram aliquots of each soil sample were Soxhlet extracted and analyzed for residual PCBs (see section 4 for methods). Results are listed in Table 17.

TABLE 17. Results of PCB Analyses of Buffalo, NY Soil
After Field Treatment - Test Area II and Untreated Controls

Ref. No.[b]	Description	Total[PCB] ppm	C_1[a]	C_1[a]
244-36-3, 4	Control, 10 days outdoors	95	13.3	14.8
	plus 12 days in container	116	15.7	17.9
244-36-1, 2	Site II treated, 10 days outdoors	145	24.8	14.4
	plus 12 days in container	160	27.4	16.7
244-38-1, 2	Control, 21 days outdoors	98	13.8	15.9
	plus 9 days in container	124	15.8	19.8
244-38-3, 4	Site II treated, 21 days outdoors	119	21.1	11.6
	plus 9 days in container	138	24.0	14.7
244-41-1, 2	Control, 53 days outdoors	137	17.5	11.0
	plus 10 days in container	128	16.4	9.4
244-41-3, 4	Site II treated, 53 days outdoors	176	24.9	17.3
	plus 10 days in container	188	27.6	15.7

a C_1 and C_2 are defined in section 4 under "Analytical Method".

b Reactions were performed in duplicate.

SECTION 7
RESULTS AND DISCUSSION

DISCUSSION OF THE RESULTS IN TABLES 1-7

The results in Table 1 using NaPEG 400-N do not differ greatly from previous results using the same reagent on water-containing soil. (See Table 2 of the progress report for January/February 1983.) This is despite the fact that reagent application conditions differed between the two experiments. In particular there appears to be a definite slowing of the reaction of remaining PCBs after the first day despite the addition of successful portions of reagent. Also, KPEG 350-1 gave much more impressive results than NaPEG 400-N (see Tables 1 and 2). Although three portions of reagent were required, the concentration of PCBs was reduced to below 50 ppm (based on the weight of extracted, dried soil) in 28 days. Addition of multiple portions of the reagent in shorter (1 hour) time intervals resulted in a reduction of PCB concentration to below 50 ppm in less than 5 days (Table 3). Comparing the results in Table 4 with the early results in Table 1, it can be seen that some improvement results when the reagent is applied under nitrogen.

In an actual spills treatment procedure, the use of a nitrogen atmosphere for reagent application is probably not practical, but efforts to limit the exposure of the soil to atmospheric moisture during mixing should also produce results superior to those in Table 2, where no such precautions were taken. The results in Table 5 were obtained using NaPEG 350-1, which is similar to KPEG 350-1, but is prepared with NaOH instead of KOH. As expected, the potassium analog is superior to NaPEG 350-1, but under similar treatment conditions the latter is superior to NaPEG 400-N, which is prepared using metallic sodium.

Pretreatment of the soil with PEGM 350 (polyethylene glycol monomethyl ether, average molecular weight 350) was done in one experiment (Table 6). The solvent should extract the PCBs from the soil and facilitate mixing with the reagent. No significant improvements in the rate of reduction of PCB concentration were observed using this method. The experiment performed using 100g of reagent (Table 7) in the first application shows a significantly greater reduction in PCB concentration after one day than the similar test using 50g of reagent (Table 2). Because the amount of water in the soil is fairly

constant (500g of soil should contain 40g of water at 8%), the 50g portion of reagent should contain a greater proportional amount of water than the 100g portion. The active nucleophiles in the 50g reagent sample are therefore more dilute and more extensively hydrated, and as a result, should be less reactive.

DISCUSSION OF THE RESULTS IN TABLES 12 AND 13

Experiments 2-4 used wet soil, that is, the soil as received containing 14.5% water. The results indicate no reduction of PCB from the starting concentration, regardless of temperature of reaction. For all other experiments in the baseline studies, the soil was dried and pulverized before addition of reagent.

The purpose of experiment 5 was to decontaminate the soil with a vigorous treatment. This series used a 5:1 weight ratio of soil to reagent. The soil was dried in open air, then pulverized with a mortar and pestle. The reagent was added through the syringe to the soil in a nitrogen glove bag; placed in an oven at 80°C; then analyzed after 1 day and 3 days. The discrepancy of results between experiments 5 and 5a may be due to the difference in temperature at time of reagent addition, 5a had cooled (to approximately 60°C) before reagent addition, and therefore the reagent did not mix as easily or thoroughly with the soil.

Experiment 6 is the same as experiment 5 except that less reagent was applied to the soil. Again, a substantial reduction in PCB's is observed after only three days.

In experiment 7, the temperature of reaction was reduced from 80°C to 65°C, all other parameters remained the same as in experiment 6. It can be seen that even with increased time of reaction the final reduction of PCB is not as great as in the experiments using higher temperature of reaction.

Experiment 8 is similar to experiment 7 except the reagent was added to the soil by a syringe. Because the syringe is injected into the soil through a small aperture in the lid of the jar, little atmospheric air comes in contact with the reagent. No adverse effect was observed by addition in air as opposed to N_2.

The objective of series experiment 9 was to determine if the effect of decreased PCB concentration with increased temperature is due to ease of mixing of reagent to soil when the soil is hot or if the increased temperature is needed for reaction. In this experiment the soil was heated to 100-115°C, the reagent was added to the soil, then the mixture was allowed to cool to room temperature and left at room temperature for the duration of the experiment. An initial decrease was observed, however further reduction was not observed with increased time.

A series of experiments was conducted using kerosene and toluene as a soil pretreatment step before addition of reagent. Solvents added to the soil before reagent application should extract at least some of the PCBs into a phase in which the reagnt is soluble. This would probably decrease the reaction time by decreasing the time necessary for complete contract of reagent and contaminant.

The procedure for experiment 10 was as follows: 100 g of air dried soil was weighed into a 4-oz. screw-cap jar, 25 ml of solvent was added to the soil (the amount of solvent necessary to wet the soil without excess), the jar was shaken on a wrist action stirrer for 15 minutes, the reagent was added by inserting a syringe filled with 10g of reagent into the soil; the jar was returned to the wrist action shaker for an additional 15 minutes, stored at room temperature, then analyzed at the appropriate time.

In experiment 10, kerosene was the solvent added as a pretreatment. An initial decrease of PCB concentration was seen after 1 day and again after 5 days. However, this trend appeared to level off with time (16 days).

The procedure for experiments A-10 and B-10 is similar to that of experiment 10 except for variations in temperature and soil to reagent ratios. The results indicate a further reduction of PCB concentration with increased temperature, (compare A-10 with 10). In addition an increase in the amount of reagent applied further reduces PCB concentration, as expected, especially at shorter time intervals (compare A-10 with B-10).

In Experiment 11, toluene was added as the pretreatment solvent. In previous laboratory experimentation of PCBs with NaPEG reagents the trend observed has been that the more halogenated PCB isomers are more easily dechlorinated than the less halogenated isomers. It can be noted in these experiments that the reduction in concentration of peak 280 is not as large as the reduction observed using kerosene. In this series there is a continued education of PCB concentration from day 5 to day 16.

A series of experiments was conducted in which the reagent was diluted in kerosene or toluene was added to the reagent prior to application of the reagent to the soil. It was determined previously that a better method of physical mixing must be developed. The objective in this case is to test the hypothesis that the reagent/solvent mixture would facilitate mixability of reagent with the soil, thereby increasing contact of reagent with PCBs. This would aid in extraction of PCBs from the soil to the reagent phase so that dechlorination would be facilitated. The addition of solvent to reagent, however, also dilutes the active nucleophiles. Once PCBs and reagent are well mixed the reaction rate should be slower than that using the concentrated reagent. Experiments 12 and 13 were designed to address these questions.

The procedure for experiments 12 and 13 was as follows: 100 g of air dried soil was weighed into a 4-oz screw-cap jar and equilibrated to 65°C. In a N_2 glove bag a 1:1 mixture of reagent to solvent was prepared and transferred to a syringe. The reagent mixture was added to the soil through a syringe in open air.

In experiment 12, kerosene was added to the reagent. After 1 day very little reduction was observed (some reduction in C_2). After 5 days, reduction had continued but was not as significant as the reagent applied alone (see experiment 7, table 12). In experiment 13, toluene was added to the reagent. The results indicate that the main effect of adding the solvent to the reagent prior to application is to dilute the reagent, thereby making it less effective than concentrated reagent.

Discussion of the Results in Tables 14 and 15

The objective of experiments 14 through 23 was to examine the parameters necessary for effective dechlorination using KPEG-350-1 reagent. In experiments 14 through 18, the soil was air dried (but not pulverized with mortar and pestle). Both the reagent and the soil were individually heated to the reaction temperature. The reagent was then added to the soil in a nitrogen glove bag, mixed thoroughly, then returned to an oven maintained at 80°C.

The parameter investigated in experiments 14 through 18 was the amount of reagent applied to the soil. In experiment 14, the weight ratio of soil to reagent was 6.7:1. This ratio was chosen since this would give an equivalent amount of potassium as in 10:1 ratio using KPEG-350 reagent (see experiments 6, 6A for comparison). The reaction temperature was held at 80°C since this was found to be the optimum temperature from previous experimentation. The results indicate that while dechlorintion did take place, it was not as effective as in those experiments using KPEG-350 reagent.

The objective of experiment 15 was to determine if successive applications of reagent would increase the dechlorination effect of PCBs. Three applications were made to the soil at one-day intervals, each with a weight ratio of 6.7:1. This resulted in a final weight ratio of 2:1 soil:reagent. A significant reduction (to < 50 ppm) was made in the concentration of PCB in soil after 2 weeks.

The objective of experiments 16 through 18 was to examine the effect of decreasing soil to reagent ratio had on the amount of dechlorination that occurs in the soil. The amount of reagent added to the soil in one application was successively increased to produce a soil to reagent ratio of 4:1, 3:1, 2:1 corresponding to experiments 16, 17, 18. The results of these experiments show clearly that the extent of dechlorination increases with an increased amount of reagent applied to the soil. A ratio of 2:1 decreases the PCB concentration in the soil to less than 50 ppm PCB in one day.

Comparing experiments 14, 15 and 18 it can also be seen that, while multiple additions of reagent do accelerate the reaction, the particular amount of reagent is most effective when added all at once.

Experiments 19 through 21 concentrated on a variety of parameters effecting reaction. In experiment 19, after reagent addition, the soil and reagent were mixed with a rotary beater for 1 hour, then returned to the oven, maintained at 80°C. No improvement is observed with increased mixing (compare to experiment 16).

In experiment 20, the soil was washed with 0.1 M KOH solution for 30 minutes then air dried before KPEG-350 addition. The reason the KOH solution was used as a pretreatment wash is as follows. It was suggested that Na^+ or Mg^+ salts in the soil, as well as other inorganic salts would possibly exchange with the K^+ in the reagent thus reducing its nucleophilicity. A strong aqueous wash prior to reagent application may exchange the salts without affecting the strength of the reagent. The results of the experiment indicate that the dilute KOH wash did not improve the percent dechlorination effected. It may be that a greater concentration of KOH is needed for efficient cation exchange, but when this experiment was attempted with a more concentrated base, the resultant soil could not be adequately air dried.

In experiment 21, the reagent was added to the soil in open air in contrast to the other experiments in which the reagent was added under nitrogen. The other reaction variables were the same as those in experiment 16. The extent of dechlorination observed in experiment 21 was actually greater than in experiment 16. Although it could not be determined why, it is worth mentioning that the reagent can be added more rapidly by the open air (syringe) method. Also, the relatively hydrous KPEG-350-1 is much less adversely affected by atmospheric moisture than KPEG-350.

Experiments 22 and 23 (Table 15) were conducted using the KOH-based KPEG-350-1 prepared in-situ, while being mixed with the contaminated soil. The reasons for preparing the reagent in-situ were to eliminate the additional reagent preparation and packaging steps, and also to take advantage of the heat generated by the reaction of KOH with the polyglycol. (For obvious safety reasons, the in-situ preparations of alkali metal-based reagents such as KPEG-350 was not considered.)

Comparing the results of experiment 22 with those of experiment 21 one can conclude that there is no major difference in the reactivity between the in-situ reagent and the one prepared before treatment. In both cases, the most of the observed decrease of PCBs occurs during the first day of reaction. A large variance in the results of the replicate tests of experiment 22 (particularly in C_1 values) may be due to poor reproducibility of mixing of the KOH and PEGM in the presence of the soil. Preparing the reagent beforehand avoids the additional source of error.

A brief reexamination of non air-dried soil was conducted using the in-situ reagent (experiment 23). This reagent is more hydrated and less hygroscopic than KPEG 350, and was used in a greater amount relative to the soil. Because of this it was thought that the water in the soil might be less of a problem. Indeed there was a noticeable decrease in PCB concentration using this treatment procedure, which is characterized by the least amount of pre-treatment preparation. The high ratio of reagent to soil (and water) is probably the main reason that there was any detectable dechlorination in this case.

Experiments 2-4 (Table 12) used the more reactive reagent, without soil pretreatment, but used a much lower reagent to soil ratio. Comparing the results of experiment 23 to those of experiment 22 (note C_2 values), however, the benefits of pre-drying the soil are still obvious.

In order to obtain results comparable to those obtained with KPEG 350, a much greater amount of the KOH-based reagent (KPEG-350-1) must be used. If a comparison is made between experiment 6, table 12 and experiment 17, table 14, it is observed that 67% more KPEG-350-1 reagent is necessary to obtain similar results in the same length of time (1-5 days). In addition, KPEG 350 reacts more rapidly after 5 days. The savings, in materials cost and treatment effort, of using KPEG 350-1 in a fieldable process must be weighed against the much greater reactivity of KPEG 350. Additional investigation is necessary for an accurate comparison of cost and effectiveness in a full-scale field treatment.

DISCUSSION OF THE RESULTS IN TABLE 16

To assess the performance of the three surfactants as the primary organic components of dechlorinating agents, the results of experiments 24-26 should be compared to those of experiment 22, where PEGM 350 (polyethylene glycol monomethyl ether, average MW 350) was used in place of the surfactant. Substantial dechlorination was observed with in-situ reagents prepared using each of the three Alnox surfactants. The in-situ reagent prepared with PEGM 350, however, was slightly more effective. The greater overall reactivity of KPEG 350-1 is most noticeably demonstrated by the greater reduction of the less reactive PCBs (note the reduction in Cl values). As with KPEG 350-1, essentially all of the measured reduction in PCB concentration occurs during the first day of mixing, when surfactant-based reagents are used.

Comparing the results of experiments 26 and 27, one can see that no improvements occur when the Alnox DD-15-based reagent is prepared beforehand. A brief attempt to examine one of the surfactants as a reagent additive was done with experiment 28. The amount of KPEG 350, and other reaction parameters were the same as in experiment B10, table 13, with the exception of the added surfactant/KOH reagent. Despite this the results were not as impressive as those obtained in the absence of the surfactant. Whether or not the Alnox DD-15 improved the soil wetting, or more importantly, reagent/contaminant contact could not be determined. The additional protic hydrogens of the surfactant and the KOH may be responsible for the slower reaction in the presence of the additive. Future experimentation with surfactants should involve reagents prepared by reacting potassium metal with a PEGM/surfactant mixture. Like KPEG 350, this reagent would be relatively aprotic. It may also be less viscous and less hygroscopic than KPEG 350.

Discussion of the Results in Tables 8, 9, 10, 11 and 17

The results of the first on-site study in Buffalo, NY (Table 17) do not give conclusive evidence of a reduction of PCB concentration in the soil after on site treatment. In contrast, laboratory experiments using untreated and field-treated soil from the same location repeatedly showed significant reductions in PCB concentration after NaPEG treatment (Tables 10 and 11). In

some cases the concentration of PCBs in the field-treated soils was actually determined to be higher than that of the control soils. In particular, the found concentration of the PCB components with lower retention times (e.g. C_1 values) was generally significantly higher for treated soils. This suggests a possible extraction problem with the untreated control soils that is less pronounced with treated soil from this site. Comparing the results in Table 8 to those in Table 9, where an experimental modification to the Soxhlet extraction procedure was used, there is preliminary evidence that the organic (polyglycol) feature of the reagent is most responsible for increasing the extraction efficiency of PCBs from this particular soil.

The field-treated samples which were subsequently treated in the laboratory (Table 11) exhibited some dechlorination, mainly between one and five days. After that, the reaction rate slowed to a level that indicated insignificant additional dechlorination by the 18th day. The reaction is evidenced primarily by the more pronounced disappearance of chromatogram peak 280 (lower C_2 values), which corresponds to the selective reduction of the more reactive PCB components. Under similar laboratory conditions, soil from the Philadelphia spill site, which had not been previously treated on site, had experienced a greater relative reduction in PCB concentration in less time. This can be seen by comparing the results of these experiments with those of experiment 6, Table 12.

The particular lot of KPEG 350-1 used in experiments (249-66-1 and 2, Table 11) contained excess base. As the reagent came into contact with the soil, some of the base appeared to precipitate out of the solution. This could account for the PCB concentration which appears to increase after a longer time. Because the reaction mixture was not continuously stirred, the extent of reaction was probably not homogeneous throughout the sample.

Discussion of Problems Encountered in the Buffalo, NY Field Study

During the field study at the Buffalo, NY site, several technical problems were encountered which have led to the acquisition of inconclusive results in complete contrast to those obtained under laboratory-controlled conditions. The point that must be stressed is that these problems, which were unforeseen at the time, are not impossible to overcome in the field. There is no reason

to believe that a direct chemical treatment of PCB-contaminated soil should not produce results at least as promising as those obtained in the laboratory studies. The Buffalo site study was, in fact, the first completed experiment which an application of reagent to contaminated soil was carried out on-site by FRC personnel.

Just before the application of the reagent to the contaminated soil, a rainfall had saturated the soil with water. All parties involved in the study agreed to proceed with the application, despite the fact that excess water was known to reduce the rate of chemical decomposition of PCBs in soil. Additional delays could have sacrificed the higher ambient temperatures of summer that were known to accelerate PCB destruction. When considering this, and the costs, in time and money involved in another rescheduling, it was decided to treat the soil as planned. Although the exact water content and organic composition of the soil was not known, prior laboratory results with other soils suggested that some measurable PCB destruction should occur. At the time, there were no previous field test results which would indicate that this study would not confirm laboratory findings.

It should be added that, given the time constraints of the site tests in the framework of the overall study, FRC was not able to provide an adequate amount of KPEG 350, which had just been selected as the best reagent formulation for dechlorination of PCBs in laboratory tests with contaminated soil. Instead, a reagent was prepared (KPEG 400-1) which was less effective than KPEG 350, but nevertheless reactive with PCBs in soil.

In the first two months following the treatment, analyses of the treated soils were obtained which indicated no significant reduction in PCB concentration in the soil. Gas chromatographic (GC) analysis showed that the individual components of the unreacted PCBs had relative concentrations similar to those published for Aroclor 1260. Nucleophilic dechlorination is evidenced not only by a reduction in the total PCB concentration, but also by a preferential reduction in the concentration of the more highly chlorinated components of the PCB mixture.

Although it is possible that sizeable portions of the total PCB contamination may be effectively shielded from the extracting solvent, the uneven distribution of PCBs in the soil is also a very probable reason for unexpected and irreproducible analytical results. As an example, rocks and small metal scraps were found in the Bengart and Memel soil, accounting for up to 75% of the total mass in some samples. These impurities should be relatively free of PCBs, except on the surface, and yet may be included in the total sample weight if small enough to pass through the sieve. In addition, the presence of PCB "hot spots" in the soil cannot be ruled out. These irregularities alone could cause considerable errors in the determination of PCBs in soil. A separate study involving dioxin-contaminated soil performed at Wright State University[7] exemplifies the importance of thorough soil homogenization to assure reproducible analytical results. The process of homogenizing, and possibly pulverizing of soil before chemical treatment is, in retrospect, strongly recommended, especially if such a treatment is for evaluation or demonstration purposes.

The lack of evidence of significant dechlorination in the field-treated soil is of much greater immediate concern than the irreproducible results and the possibility of liberation of additional "trapped" PCBs by the reagent. PCB dechlorination occured to a considerable extent with the Buffalo site soil in preliminary experiments conducted in FRC's laboratory (see Table 10). KPEG 350, in particular, reduced the levels of PCBs in the contaminated soil from approximately 100 ppm to below 50 ppm. Subsequent laboratory experiments were conducted using soil which had been taken from the chemically treated plot nine months after on-site treatment. The composite soil sample which was removed in May 1984 was homogenized, divided into portions and subjected to additional reagent applications under various laboratory conditions. In each case, substantial dechlorination occurred, as evidenced by a considerable reduction in the total PCB concentration. As expected, the reduction was greatest for the more highly chlorinated PCBs. By this time, several methods were proposed for heating the soil in the field in order to accelerate the chemical decomposition of soil contaminants. In addition, and perhaps more importantly, it was discovered by this time that pre-drying was

essential for the reagent to be effective. Results using PCB-contaminated soil from the Philadelphia, PA site showed that significant dechlorination is achieved by simply air drying the soil at room tempeature prior to the application of the reagent. Without this pretreatment, insigificant decontamination was observed for the relatively wet soil, even when KPEG-350 was used (see section 5).

When the soil sample was obtained from the site in May 1984 it was noticed that the treated soil was still very wet. Also, water condensation was observed under the plastic sheet that covered the plot. The sheet may keep the rain out, but it also tends to keep moisture in. This was probably not a major disadvantage, however, because without the cover, all but the soil particles closest to the surface would retain most of their excess moisture, even in extremely dry atmosphere. In light of this, thorough mixing of the soil in air, prior to reagent application should be an essential, minimum pretreatment. Excess water, if not adsorbed water, can be easily removed by exposing all of the soil to the surface, even at ambient temperatures. If such a treatment is performed on-site, especially on a warm, dry day, the promising results obtained in the laboratory tests will undoubtedly be verified. At this time, the various inhibiting effects of water are the only known major problems which have adversely affected the results of this initial field study. Air drying is a very important step which should greatly minimize these effects in field tests. The on-site treatment of soils contaminated with PCBs and other halogenated aromatics still looks very promising, based on the results obtained in the laboratory studies. There is, of course, considerable work that remains to be done in the area of process development, particularly with respect to optimizing conditions for soil decontamination. Various solvent pretreatment and soil heating methods, for example, deserve additional and scaled-up investigation. Some of these techniques are currently being studied in the laboratory. Field testing must continue, however, not only to verify laboratory results, but to provide the first-hand experience in real-world situations that is necessary for the development of a total fieldable process.

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APPENDIX A
MATERIALS AND EQUIPMENT USED IN THIS STUDY

Gas Chromatograph

Hewlett Packard Model 3380A equipped with a Model 5700A integrator, a Ni^{63} electron capture detector and a 6' and 1/4" OD silanized glass column of 3% OV-1 on 80-100 mesh Supelcoport. Operating conditions were: 90% Argon - 10% Methane carrier at 33 ml/min. Temperatures were: column, 195°C; injector, 250°C, detector, 300°C.

Raw Materials

Carbowax polyethylene glycol 400 (PEG 400) was obtained from Quaker City Chemical Co. Poly(ethylene glycol monomethyl ether) 350 (PEGM 350) was obtained from Aldrich Chemical Company. Other chemicals used to manufacture the reagent or in sample preparation were obtained from various suppliers.

APPENDIX B
SAMPLE NUMBERS FOR EXPERIMENTS SUMMARIZED IN TABLES 12-16

Expt.	Sample No.	Analysis No.
2	249-47-1	244-50-5
2a	249-47-2	244-50-6
3	249-47-3	244-50-3
3a	249-47-4	244-50-4
4	249-47-5	244-50-1
	249-47-5	244-50-1A
4a	249-47-6	244-50-2
5	249-47-9	244-54-1
	249-47-9	244-54-3
5a	249-47-10	244-54-4
	249-47-10	244-54-4
6	249-50-3	244-57-3
	249-50-3	244-57-3A
	249-50-3	244-57-3B
6a	249-50-4	244-57-4A
	249-50-4	244-57-4A
	249-50-4	244-57-4B
7	249-47-7	244-53-1A
	249-47-7	244-53-3A
7a	249-47-8	244-53-2A
	249-47-8	244-53-4A
8	249-50-5	244-57-5
	249-50-5	244-57-5A
	249-50-5	244-57-5B
8a	249-50-6	244-57-6
	249-50-6	244-57-6A
	249-50-6	244-57-6B
9	249-50-1	244-57-1
	249-50-1	244-57-1A
	249-50-1	244-57-1B
9a	249-50-2	244-57-2

Expt.	Sample No.	Analysis No.
10	249-55-1	244-61-1 244-61-1B 244-61-1C
10a	249-55-2	244-61-2 244-61-2B 244-61-2C
11	249-55-3	244-61-3 244-61-3B 244-61-3C
11a	249-55-4	244-61-4 244-61-4B 244-61-4C
12	249-55-5	244-61-5 244-61-5B
12a	249-55-6	244-61-6 244-61-6B
13	249-55-7	244-61-7 244-61-7B
13a	249-55-8	244-61-8 244-61-8B
A-10	279-13-1	279-13-1 279-13-1A
A-10a	279-13-2	279-13-2 279-13-2A
B-10	279-13-3	279-13-3 279-13-3A
B-10a	279-13-4	279-13-4 279-13-4A

Expt.	Sample No.	Analysis No.
14	249-71-1	249-71-1
	"	249-71-1A
	"	249-71-1B
14a	249-71-2	249-71-2
	"	249-71-2A
	"	249-71-2B
15	279-1-1	279-1-1
	"	279-1-1A
	"	279-1-1B
15a	279-1-2	279-1-2
	"	279-1-2A
	"	279-1-2B
16	249-71-3	249-71-3
	"	249-71-3A
	"	249-71-3B
16a	249-71-4	249-71-4
	"	249-71-4A
	"	249-71-4B
17	279-1-3	279-1-3
	"	279-1-3A
	"	279-1-3B
17a	279-1-4	279-1-4
	"	279-1-4A
	"	279-1-4B
18	279-1-5	279-1-5
	"	279-1-5A
	"	279-1-5B
18a	279-1-6	279-1-6
	"	279-1-6A
	"	279-1-6B

Expt.	Sample No.	Analysis No.
22	279-6-1	279-6-1
	"	279-6-1A
	"	279-6-1B
22a	279-6-2	279-6-2
	"	279-6-2A
	"	279-6-2B
23	279-6-3	279-6-3
	"	279-6-3A
	"	279-6-3B
23a	279-6-4	279-6-4
	"	279-6-4A
	"	279-6-4B
24	279-14-1	279-14-1
	"	-1A
	"	-1B
24a	279-14-2	279-14-2
	"	-2A
	"	-2B
25	279-14-3	279-14-3
	"	-3A
	"	-3B
25a	279-14-4	279-14-4
	"	-4A
	"	-4B
26	279-14-5	279-14-5
	"	-5A
	"	-5B
26a	279-14-6	279-14-6
	"	-6A
	"	-6B
27	279-45-1	279-45-1
	"	-1A
27a	279-45-2	279-45-2
	"	-2A
28	279-45-3	279-45-3
	"	-3A
28a	279-45-4	279-45-4
	"	-4A

APPENDIX C
SOIL PRE-TREATMENT TECHNIQUES USED IN LABORATORY TESTS

A - Soil air dried and pulverized prior to treatment.

B - Soil dried and pulverized - soil heated to 100-115°C - reagent added reacted at room temperature.

C - Soil air dried 25 ml kereosene added prior to reagent application.

D - Soil air dried 25 ml toluene added prior to reagent application.

E - Soil air dried.

F - Soil air dried. Reagent and soil heated to reaction temperature. Reagent added under N_2.

G - As in "F", two more portions of reagent added after 1 and 2 days respectively.

H - As in "F", but with 1 hour of initial mixing.

J - As in "F", but soil was washed for 30 minutes with 100 ml of 0.1M KOH before drying.

K - As in "F", but Reagent added in air.